

PLASTICS PYROLYSIS AND COAL COPROCESSING WITH WASTE PLASTICS

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ABSTRACT

Pyrolysis of waste plastics is one of the routes to waste minimization that has been gaining in interest in recent times. A compact unit is designed that can pyrolyze a mixture of waste plastics and used oil. The product of the process is a liquid oil that has considerably reduced viscosity and which can be either used as fuel directly or as a feedstock for refineries. Pyrolysis was carried out for the waste oil alone and for its mixture with plastics of one type (HDPE). Different temperatures of reaction and the product viscosities related to the temperatures of operation. Residence times were as low as 2-8s. The reactor was divided into two parts, the first part at the inlet was deliberately kept at a lower temperature to first bring up the Reynolds numbers ($>15,000$) to high values before introduction to the high temperature second section.

The liquid product of pyrolysis can be used for the co-liquefaction of coal. Several coal liquefaction studies were carried out to determine the effect of the use of the waste plastic-used oil product of pyrolysis as solvent. The results indicate considerable enhancements of the conversions and selectivities of coal for such prepyrolyzed liquid.

Introduction

Plastics form a major portion of all municipal wastes. It was reported (1) that some 30 billion pounds of plastic waste are generated in the US per year. Also the demand for plastics would reach 76 billion pounds by the turn of the century. Currently, only about 1% of the plastics waste is recycled. The recycling of the plastic can be costly and difficult because of the constraints on water contamination and inadequate separation prior to recycling.

Therefore several new processes are currently under development for the treatment of waste plastics. Two processes have shown promise, pyrolysis and hydrolysis, in recovering the basic chemicals and fuels from the waste plastics. In pyrolysis, the plastics are heated in the absence of oxygen in a closed environment, with the resulting products of pyrolysis available for use as a chemical feedstock, or fuel. Hydrolysis decomposes plastic wastes through a series of chemical reactions. These new processes will reduce the cost of monomers and the consumption of petroleum. In one instance, scientists have demonstrated a new process for sequential pyrolysis for waste carpet recycling. In this case caprolactum, the starting material for nylon production, was separated with yields of around 85% without separating the nylon from the backing material of the carpet. It is reported that a commercial plant could produce high grade caprolactum at a cost of \$0.15-0.50/lb compared to the commercial cost of \$1.00/lb. Thus costs could be reduced by as much as 50%. Thus pyrolysis appears to be an attractive alternative to plastics landfilling or incineration.

Many companies are already showing considerable interest in pyrolysis of waste plastics. The Japanese company, Fuji has started a commercial scale plastics to gasoline plant at Aioi, that is capable of processing 11 million lb/yr of waste plastic. In this process the plastic is first preheated to 250°C. The preheated plastic is then fed by an extruder to a furnace, and then to a cracking unit that uses aluminosilicate catalyst. The process yields 40% gasoline, 20% kerosene, 20% gas-oil mixture, 15% gas and 5% residuals. Retrieved energy is used to power the plant. Annually the plant would produce one million gallons of gasoline (2).

Chuo Kagaku Co., the largest PS food tray manufacturer in Japan has a 2-million-lb/yr plant for reclaiming PS waste that is based on the Fuji design. The plant is anticipated to yield on startup, a fuel mixture of 90% aromatics, 6% paraffins and 4% olefins. When blended with gasoline, it produces a high octane fuel.

Amoco Chemical, Chicago, is also concentrating on the development of a pyrolysis unit. Scientists at Amoco have concluded that use of a small scale pyrolysis unit to crack mixed plastics into liquid chemical prior to feeding them to a refinery unit appears to be the optimal route. Liquids being easily transportable, this would avoid the costly step of shipping bulk plastic scrap to far-flung U.S. oil refineries (2). Also in the U.S., the American Plastics Council, Washington, DC, is sponsoring two pyrolysis projects by recycler Conrad Industries, Chehalis,

WA. One of the plants is already on stream. A drum of the pyrolyzed plastic oil (PPO) of this company was obtained and was used in the coal coprocessing experiments as indicated in Table 2. Typical composition of household wastes is shown in Table 1.

System Design

The new compact pyrolysis unit has been designed to pyrolyze a mixture of waste molten plastic and waste oil. This unit operates at very low residence times (2-8 seconds) and can operate continuously. The reactor consists of a 125 ft long 2.5 mm diameter S.S. tube that is divided between two different heating or reaction sections. The temperatures of operation can be finely controlled so as to give liquid products of various viscosities. The temperatures of operation range from 350-600°C, the pressures are low (ambient) to medium (100-300 psi). The reaction is carried out in two stages. In the first reactor tube section the temperatures are kept low (300-400°C) to allow the viscosity to reduce sufficiently to give high Reynolds numbers in the subsequent high temperature (450-600°C) section. As a result, Reynolds numbers higher than 15,000 are obtained in this section. A detailed schematic of the process is included. Two sand baths are used for the liquefaction process and the temperatures of the two are set independently to give the required temperature steps in the operation.

The feed liquid which consists of waste oil and waste plastics (which is kept molten) at 250-300°C are subjected to nitrogen pressure to push the liquid through the cracking sections. The tube outlet pressure can be controlled by means of a back pressure regulator that can be adjusted to any required set point. Thus complete variation in operational pressure is possible. The reaction can be carried out at different pressures and the effect of operation pressure can be investigated almost independently of the residence times.

Several runs of pyrolysis with waste oil were carried out in the laboratory. Two typical temperature profiles are included and the corresponding viscosities of the product are also included in the figures.

Decomposition temperature ranges of the plastics are usually obtained from thermogravimetric methods (4). These methods have been used by other investigators for obtaining the reaction rate parameters, i.e., the pre-exponential factors and the activation energies. These constants are used in the present experiments to decide on the residence time variations that would be necessary to treat plastics of different compositions and also to predict the properties of the products where possible, using model based simulation.

Several pyrolysis runs were carried out with plastics dispersed in the oil and the pyrolysis products obtained. The temperature profile for one run with 2.5% HDPE pellets are included.

Results and Discussion

Once the pyrolysis products of the plastics are obtained, they can be used to carry out the liquefaction of the coal in a batch or continuous manner. Here, the results of tubing bomb experiments based on batch coal coprocessing show that the reaction of liquefaction occurs to increased levels of conversion with the addition of (waste) plastics, such as polystyrene or HDPE. Increases in conversions of around 20% are obtained with the unpyrolyzed waste plastics, and selectivities are enhanced by 15-25% on an average. The conversions further increase if the plastics and the waste oil solvents are in addition prepyrolyzed (two stage liquefaction). This is the basis for the design of the pyrolysis section followed by the coal coprocessing.

The main design parameters are the residence time, feed temperature, the two stage temperatures, and the flow inducing pressure difference. These parameters have to be very carefully chosen in order to get the right conversions and yields of liquids. The effects of temperature and residence times are relatively well understood for the pyrolysis reactions. Too high a residence time results in excessive gas formation and when the temperatures are high to high coke formation. The temperatures that are attainable in any pyrolysis unit thus determines the yields of gas, liquids and coke. Usually the threshold temperatures for pyrolysis depends on the type of material to be processed. In general the lower limit of temperature for most pyrolysis is 350-400°C. The actual temperatures chosen are usually much above this. Since thermal cracking reactions proceed with significant activation energies, temperatures has an important effect on rate. Activation energies are in the range of 55-65 kcal/mol (6).

Temperature is also known to have a very important effect on the selectivities of paraffin pyrolysis. In the present case the aim is to maximize the formation of liquids and therefore the temperatures are lower, of the order of about 500-700°C. The exact temperature chosen would then depend on the nature of the material to be processed. If the feed material is simply waste lubricating oil, then the temperatures of 450-500°C are found to be sufficient for the maximization of liquids. If in addition we are adding waste plastics then the temperature of cracking must usually be raised in order to bring about sufficient chain scission and obtain products in the liquid form suitable for use as liquid fuels or as feed to a refinery unit.

Conclusions

Exploratory batch reaction studies have shown two-stage coal coprocessing with waste plastics and oils to yield high conversions of coal (>80%) with a high selectivity for oil (>60%). the waste oils and plastics were first thermally cracked in a first stage to yield a liquid solvent for the second-stage coal coprocessing. A pilot scale unit was constructed for performing the first stage cracking studies. Waste oil mixed with HDPE were successfully cracked using this unit, there being no significant amounts of coke or solids produced.

The use of low residence time cracking would offer a number of advantages. Two of these are (1) transportation costs could be significantly reduced by removing contaminants close to the generation site and by reducing the bulk density of the plastics; and (2) handling of waste plastics/oils during coal coprocessing would be simplified due to the low viscosities and fluidic properties of the cracked products.

References

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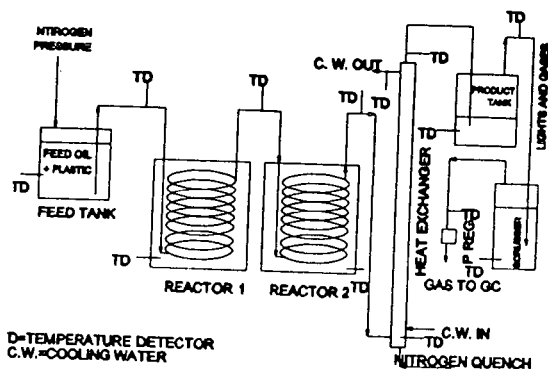


Figure 1: Pyrolysis Unit

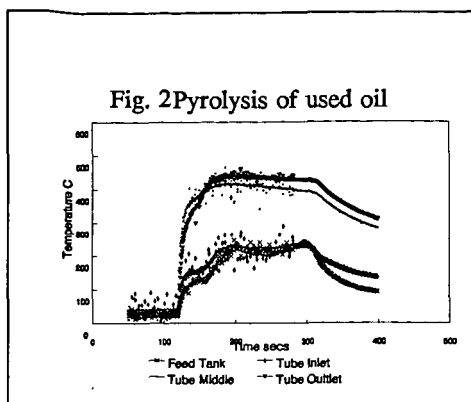


Figure 2. Pyrolysis of waste oil of viscosity 275 cSt to give product of viscosity 50 cSt

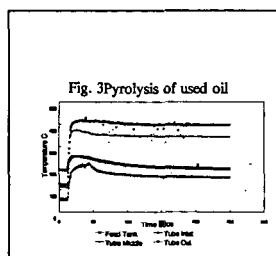


Figure 4. Pyrolysis of waste oil of viscosity 275 cSt to give product of viscosity 130 cSt

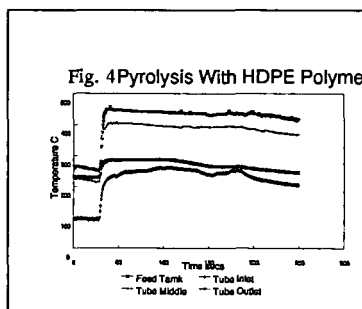


Figure 3. Temperature Profile for Pyrolysis of HDPE (2.5%) Dispersed in Used Oil, Product Viscosity was 80cSt @30°C

Table 1. Composition Of Mixed Plastics Wastes:

Composition (% wt)	
Polyethylene	60
Polypropylene	05
Polyvinylchloride	10
Polystyrene	15
Polyethyleneterephthalate	05
Polyamide	05

Table 2. Response of coal conversion /selectivity to addition of pyrolyzed plastic , PS & waste oil

Solvent	Hexane Convrsn(%)	Total Convrsn(%)	Selectivity(%)
Waste Oil	43	73	59
Waste Oil/polystyrene(PS) 1:1	39	60	65
Prehydrocracked waste oil	60	86	70
Waste oil/PS prehydrocracked1:1	63	97	65
Pyrolyzed plastic oil(PPO)	64	91	70
Prehydrocracked PS/waste oil 1:1	73	100	73
PPO/waste oil 1:1	56	81	69

Reaction conditions: 2.5g DECS-6 coal, 10g solvent, 0.25g Fe_2O_3 , 425°C, 1250 psig H_2 , 1 hour